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THE FLOW AND FRACTURE OF ZONE REFINED TUNGSTEN

Technical Report WAL TR 834.2/11-2

by

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ABSTRACT

Zone-refining efforts have been directed toward enhancing the control of the zone. These efforts have included additional coil designs, effect of atmosphere gas velocities, and zone-refining while power fluctuations were at a minimum. Resistivity ratios have been determined on two as-received electron-beam zone-refined single crystals of tungsten. A description of the measuring apparatus and the values obtained are presented. A technique for measuring resistivities by an eddy-current method is described briefly.

INTRODUCTION

During the period covered by this report, most of the experimental work was devoted to the final testing of the apparatus to be used for zone-refining and to the instrumentation for and measurement of the resistivity of the tungsten specimens to be zone-refined. The zone-refining apparatus appears to be quite satisfactory to commence the zone-refining of the electron-beam zone-refined tungsten single crystals. Residual resistivity measurements have been made on the as-received tungsten specimens, but poor results at liquid helium temperatures are requiring a closer look at the technique presently employed.

ZONE REFINING EFFORTS

Several new melting coil configurations have been tried because of some of the difficulties encountered in controlling the width of the zone with the coil presently in use (3-high, single turn). Efforts have been aimed at reducing the stable zone width. It has already been established that single turn coils less than 3-high would not produce a molten zone with the power presently available. The new coil designs tried were (1) 3-turn, one high, and (2) 2-turn, two high. Neither of these designs allowed us to melt a zone in the tungsten even at full power. Two other designs which will be tried are (1) 3-turn, two high, and (2) 4-turn, one high. These will cover all of the designs possible within the restrictions of our task except for the possibility of conical "levitation" coils.

Past efforts on test bars zoned during ordinary working hours indicated that our control was jeopardized by power fluctuations both within the building and in the line coming into the building. In order to assure ourselves that we could control the zone if there were minimum fluctuations, a test bar was melted at night, starting at 8:00 P.M. when

there were no other variable power requirements in the building. This proved successful, considerably increasing our control of the zone.

Another source of difficulty was the heavy condensation of volatile materials on the inside surface of the specimen tube. The condensation is quite opaque and limits observation of the zone. Since volatilization is more or less constant, it was hoped that the condensation could be displaced to a position on the specimen tube whereby our visual observation of the zone would be enhanced. This is normally accomplished, in closed system zone refining operations, by having a gas circulate through the system by convection. A glass "down leg" is provided (usually cooled) to assist the convection of heated gasses in the melting tube. In passing over the molten zone, the gas sweeps volatilized materials to a region above the zone. It was felt that perhaps the design of the apparatus as originally presented (see Figure 1, Report Q-B1973-2) did not permit the gas (purified argon) to flow sufficiently fast to sweep out the evaporated material.

An open-tube system was used to determine the effect of increased gas velocity on reducing or displacing the condensation from the region around the molten zone. A zone was formed in a tungsten rod and purified argon passed through the system at various flow rates from 0 to 3 cubic feet per hour. The maximum rate is quite high, corresponding to a gas velocity of approximately 50 ft./min. Even at the highest flow rate the condensation still formed heavily on the specimen tube above the zone.

It should be pointed out that while these experiments were done in an attempt to reduce the condensation and enhance the visibility of the zone and were not successful, actual control of the zone during melting is accomplished by looking up at the zone from below the coil, since the condensate does not form (at least to the degree of visibility impairment) on the glass below the coil.

RESISTIVITY RATIO MEASUREMENTS

Low temperature resistance measurements as a means of studying impurity distributions in zone-refined ingots of metals have been described by Kunzler and Wernick[1]. The advantage of this method is that an evaluation of the purity of a sample can be made without destroying it or its geometry. Its disadvantage is that the results are not specific or quantitative, and only show the total effect on resistivity of all the impurities present, at least as far as electrically active impurities are concerned. However, at the purity levels developed by zone-refining, quantitative detection of individual impurities cannot usually be achieved by presently known techniques.

The circuit employed for the measurement of the electron-beam zone-refined specimens is shown in Figure 1. Tungsten wire leads are spot-welded at intervals onto the tungsten rod, and the free ends of the tungsten wire leads tinned with silver-solder. Enameled copper wires are soft-soldered onto the silver-solder and thence to the galvanometer. Heavy copper wires carry the current to binding posts on the ends of the specimen rod. A specimen prepared for measurement is shown in Figure 2. The lower five probes are welded to that portion of the rod which has been electron-beam zone-refined and is a single crystal. The upper two probes are on the polycrystalline "base metal" ends of the rod.

For the actual measurement of the resistance, a direct current is passed through the specimen in one direction and the voltage drop across any pair of probes is measured using a Rubicon 3-dial potentiometer with a sensitivity of approximately 0.02 μV. The current is supplied by three 2-volt storage battery cells connected in parallel and is determined accurately by measuring the voltage drop across a 0.001 ohm Leeds and Northrup standard resistor. A wound nichrome loading resistor immersed

[1] Kunzler, J. E. and Wernick, J. H., Trans. AIME, 212, No. 6, pp. 856-860 (1958).

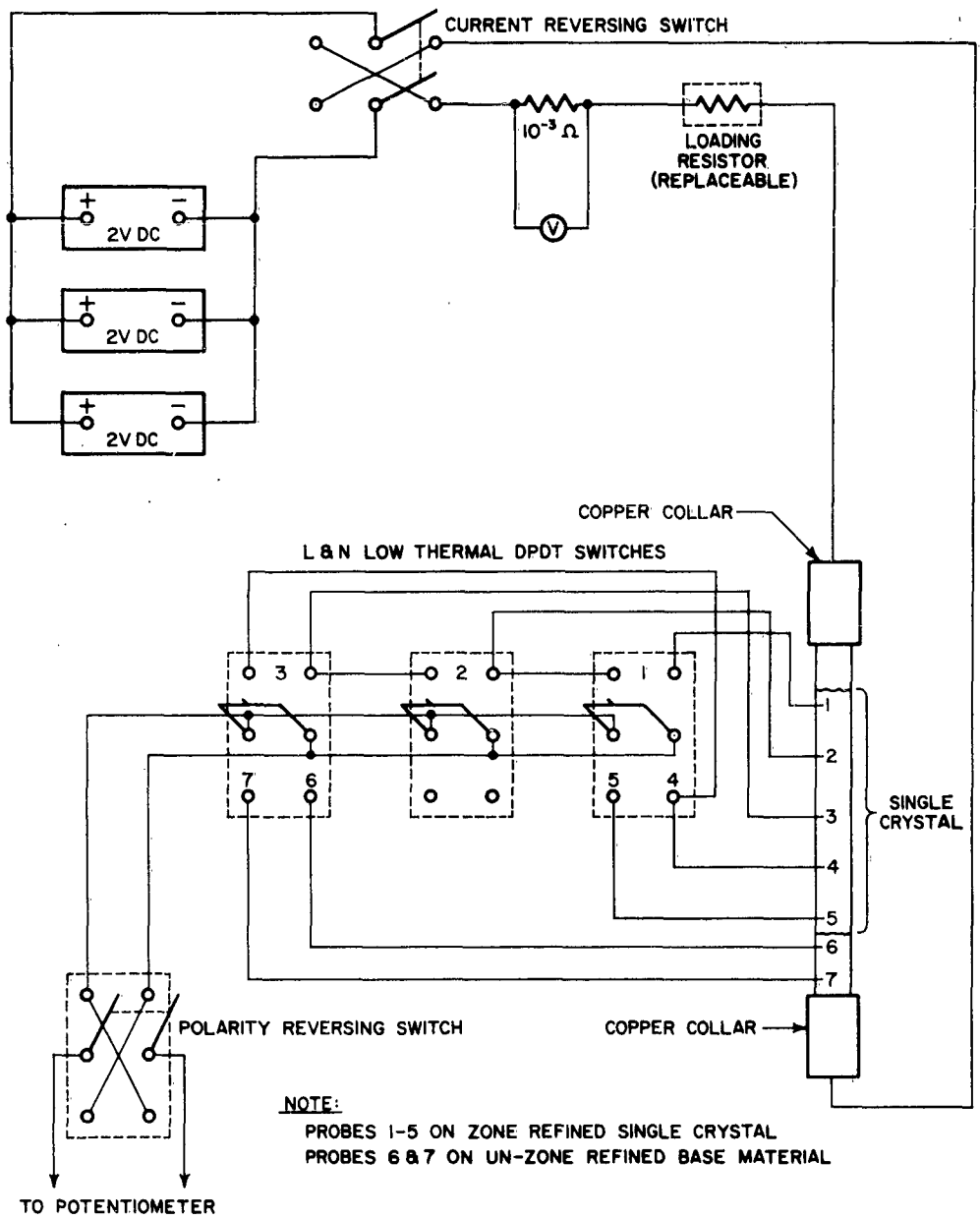

FIG. 1. CIRCUIT DIAGRAM FOR MEASURING RESISTIVITY RATIOS

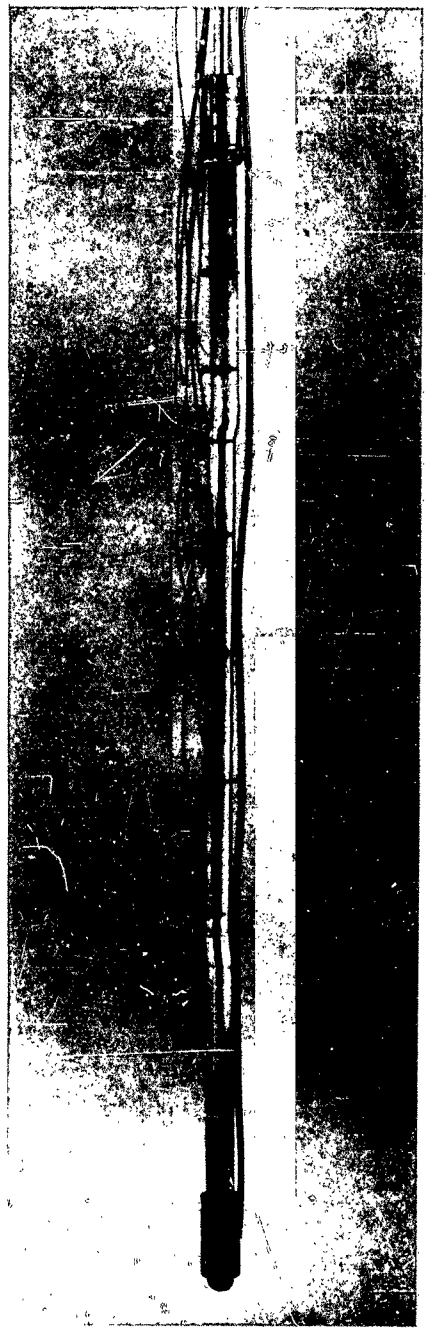

FIG. 2. SPECIMEN PREPARED FOR RESISTANCE MEASUREMENTS

in an oil bath is used to limit the current flowing in the circuit. This resistor is replaceable so that the current may be increased or decreased as the resistance of the specimen is increased or decreased depending on the measurement temperature. Leeds and Northrup low thermal EMF switches, copper wiring, and draft shields were used to minimize extraneous EMF contributions to the potential readings. These extraneous EMF's could not be entirely eliminated, but were compensated for by reversing the current direction and again determining the voltage drop between probes. Since the extraneous EMF's do not change direction or value (assuming all conditions remain the same, except the impressed current) they are effectively eliminated by using the average of the sum of the voltage drops between probes.

While this technique specifically measures resistance between probes, by measuring this resistance at various temperatures and using the ratio of the resistances at the different temperatures, we arrive at a resistivity ratio. This is true, however, if we use the assumption that the geometry of the specimen is not changed (or to only a negligible amount) by changes in temperature.

Tables I and II list the data and results of the resistance measurements on two electron-beam zone-refined tungsten specimens. In both tables, probes 6-7 are on the polycrystalline ends of the sample and all other probes are on the single crystal portion. It is noted in Table I at liquid helium temperatures that some of the measured voltages have a minus sign. This indicates that the voltage drop across those pairs of probes is opposite to the applied voltage. The resistivity ratios involving those particular probe pairs are quite high (approximately 10,000 or higher) indicating that the electron beam refined material is already quite pure and should be an excellent starting material for the induction zone refining efforts. When no current was passed through the sample these same probes indicated a potential. This potential is apparently due to a small, but significant, Seebeck effect caused by compositional differences in the probe circuits.

Table I

RESISTANCE AND RESISTIVITY RATIO MEASUREMENTS ON SAMPLE W-1

Specimen Temperature, °K		Pairs of Probes 1-2	2-3	3-4	4-5	6-7
295 (Room Temperature)	Voltage, μV, Forward	61.95	62.12	57.45	45.50	44.49
	Current, amps	1.013	1.013	1.013	1.013	1.013
	Resistance, μΩ	61.16	61.32	56.71	44.92	43.92
	Voltage, μV, Reverse	62.04	62.62	57.82	45.14	44.47
	Current, amps	1.013	1.013	1.013	1.013	1.013
	Resistance, μΩ	61.24	61.82	57.08	44.56	43.90
	Average Resistance, μΩ	61.20	61.57	56.90	44.74	43.91
77 (Liquid Nitrogen)	Voltage, μV, Forward	34.34	33.74	31.25	25.00	26.64
	Current, amps	5.379	5.374	5.374	5.374	5.372
	Resistance, μΩ	6.38	6.28	5.82	4.65	4.96
	Voltage, μV, Reverse	34.08	33.84	31.40	24.57	26.67
	Current, Amps	5.369	5.369	5.366	5.366	5.366
	Resistance, μΩ	6.35	6.30	5.85	4.58	4.97
	Average Resistance, μΩ	6.37	6.29	5.83	4.62	4.97
4.2 (Liquid Helium)	Voltage, μV, Forward	1.02	-.05	.17	.18	4.96
	Current, amps	13.179	13.153	13.075	13.139	13.038
	Resistance, μΩ	.077	.004	.013	.014	.380
	Voltage, μV, Reverse	0	.08	-.08	.67	4.67
	Current, amps	12.967	12.956	12.936	12.993	13.030
	Resistance, μΩ	0	.006	.006	.052	.358
	Average Resistance, μΩ	.039	.001	.003	.033	.369
Resistivity Ratio	$\rho_{295°K}:\rho_{77°K}$	9.61	9.79	9.75	9.69	8.84
Resistivity Ratio	$\rho_{295°K}:\rho_{4.2°K}$	1581	61,570	18,967	1368	119

Table II

RESISTANCE AND RESISTIVITY RATIO MEASUREMENTS ON SAMPLE W-2

Specimen Temperature, °K		Pairs of Probes 1-2	2-3	3-4	4-5	6-7
300 (Room Temperature)	Voltage, μV, Forward	65.35	60.02	62.34	62.81	49.78
	Current, amps	1.048	1.048	1.048	1.048	1.048
	Resistance, μΩ	62.36	57.27	59.48	59.93	47.50
	Voltage, μV, Reverse	65.07	60.07	62.66	62.54	49.78
	Current, amps	1.048	1.048	1.048	1.048	1.048
	Resistance, μΩ	62.09	57.32	59.79	59.68	47.50
	Average Resistance, μΩ	62.22	57.29	59.63	59.80	47.50
77 (Liquid Nitrogen)	Voltage, μV, Forward	34.99	31.74	33.03	33.42	30.94
	Current, amps	5.280	5.283	5.286	5.286	5.290
	Resistance, μΩ	6.63	6.01	6.25	6.32	5.85
	Voltage, μV, Reverse	34.88	32.03	33.37	33.15	30.90
	Current, amps	5.283	5.283	5.283	5.283	5.283
	Resistance, μΩ	6.60	6.06	6.32	6.27	5.86
	Average Resistance, μΩ	6.61	6.03	6.28	6.29	5.85
4.2 (Liquid Helium)	Voltage, μV, Forward	.17	Probes Broke			8.71
	Current, amps	14.976				14.990
	Resistance, μΩ	.0114				.581
	Voltage, μV, Reverse	.13	Probes Broke			9.19
	Current, amps	14.852				14.870
	Resistance, μΩ	.00875				.618
	Average Resistance, μΩ	.0101				.602
Resistivity Ratio	$\rho_{300°K}:\rho_{77°K}$	9.41	9.50	9.50	9.51	8.12
Resistivity Ratio	$\rho_{300°K}:\rho_{4.2°K}$	6160	-	-	-	79

The significance of these very small error voltages is appreciable when it is realized that at such a low temperature (4.2°K) the resistance of the zone-refined specimen is so low that the voltage drop between probes is near, and perhaps below, the sensitivity of our measuring circuit. This difficulty could be overcome by increasing the current through the specimen. However, the problem then arises of the effect of the increased Joule heating of the specimen. Another possibility is to increase the spacing between probes. This would, however, create an additional discrepancy since the resistivity of the zone-refined length varies with length and we would be measuring an averaged resistance over the measured length.

To overcome the difficulties described for measurements at 4.2°K we are looking into the possibility of another and more advantageous technique. This technique, called the "eddy-current method[2]", involves measuring the rate of decay of flux from a bar in an external magnetic field that has been rapidly reduced to zero. The sample rod is wound locally with a small secondary (pickup) coil and the whole inserted in a larger magnetizing solenoid. A step function of current is applied through the magnetizing coil, and the resulting voltage across the pickup coil is noted as a function of time. This voltage is caused by the penetration of flux into the rod. If now the external field is suddenly interrupted, the flux emerging from the rod will reduce to zero. This flux reduction is due to the decay of the eddy currents induced in the rod by the external field. The rate of decay of the eddy currents is in turn a function of the resistivity of the material through which the eddy currents are moving. The exact derivation of the relationships involved are presented quite amply in the cited reference. This measuring technique is theoretically capable of measuring residual resistivity ratios as high as 100,000. Another advantage of the technique as applied to our particular problem is that no connections need be made to the sample, thus eliminating the extraneous EMF's previously described. The apparatus required for these measurements is on-hand, having been built for similar measurements

[2]Bean, C. P., DeBlois, R. W., and Nesbitt, L. B., J. Appl. Physics., 30, No. 1, 1976-1980 (1959).

on zone-refined beryllium. One sample of the electron-beam zone-refined tungsten was measured by this technique at room temperature and the resistivity agreed within 3% of the value obtained by the voltage-drop method. The difference is really insignificant since it is the ratio of resistivities which is the desired parameter. We are now attempting to utilize this equipment for our measurements at the low temperatures.

FUTURE WORK

We have already indicated in the section on our zone refining efforts that we have two other coil designs to test. These will be a 3-turn, two high coil and a 4-turn, one high coil. We will then be ready to go ahead with the zone-refining of the electron-beam zone refined single crystals.

The eddy-current method of determining resistivity ratios will continue to be developed in an effort to apply it to our particular problem of measuring extremely low resistivities at low temperatures.

As the initial phase of our mechanical testing program, a section will be cut out of one of our as-purchased tungsten single crystals and tested in tension. This is necessary so that we may fairly evaluate the results of our purification efforts. We do feel, however, that since both of the crystals on-hand have essentially the same thermal history, the testing of one of the crystals will provide a satisfactory evaluation of our starting stock.

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Approved by:

H. G. F. Wilsdorf

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